

PERMEABLE REACTIVE BARRIERS: APPLICATION TO ABANDONED MINE LAND RECLAMATION IN UTAH¹

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Abstract. Historical uranium exploration, mining, and milling operations have resulted in elevated uranium (U) concentrations in many aquifers throughout Utah and other Western states. Zero-valent iron permeable reactive barriers (ZVI PRBs) may represent a cost-effective technology for removal of U and other contaminants from ground water on State and Federally managed lands; however, little is known about the long-term performance of ZVI PRBs. Hydrologic and biogeochemical data have been collected for 10 years from a ZVI PRB installed in a U-contaminated aquifer near Fry Canyon, Utah. During the 10 years of continuous operation, more than 99 percent of the input U was removed from the groundwater (input U concentration can exceed 10,000 micrograms per liter). Ionic tracer tests indicate a decrease in ground-water velocities in the PRB, from an average of 1.54 meters/day (m/d) in 1999 to 0.95 m/d in 2003 and 0.4 m/d in 2005. Increased amounts of mineral precipitation and/or hydrogen gas production and entrapment could be causing the observed reduction in flow velocities. The total dissolved gas (TDG) pressure of selected wells within the ZVI PRB increases by over 100 mm Hg relative to the upgradient wells outside of the PRB, potentially indicating the build up of hydrogen gas. Gas samples collected from wells upgradient and within the ZVI PRB are currently (2006) being analyzed for the amount of dissolved hydrogen, as well as other gases. Since the installation of the ZVI PRB, increasing proportions of influent sulfate has been removed. The increasing sulfate removal efficiencies are probably a function of bacterially mediated sulfate reduction. The isotopic enrichment of the stable isotopes of sulfur and oxygen in the sulfate anion from groundwater samples collected within the ZVI PRB support the presence of bacterially mediated sulfate reduction. Increased amounts of bacterially mediated sulfide production in the ZVI PRB would likely remove other trace metals, if present in the input water, by the formation of metal sulfides.

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Introduction

Permeable reactive barriers (PRBs) may represent a viable tool for remediation of metal-contaminated groundwater associated with abandoned mine lands (AML) on State and Federally managed properties. There are more than 25,000 inactive mine sites in the western United States and numerous exploration prospects, many of which are on Federal lands (U.S. Geological Survey AML Science Team, 1999). Many AML sites are in remote areas, therefore, low maintenance remediation technologies, such as PRBs, are especially useful. A PRB can be installed in shallow aquifers (< 5 m below land surface) with commonly available construction equipment that is easily transported to remote sites. PRBs have no energy or short-term maintenance requirements, therefore, the costs typically associated with running power lines and maintaining equipment for above-ground treatment technologies are not incurred. The PRBs treat contaminated groundwater below the land surface, which eliminates visual impacts from the use of equipment on the land surface (fig. 1). Damage from vandalism, livestock, and wildlife to above-ground remediation infrastructures does not occur with PRBs.



Figure 1. Permeable reactive barrier treating uranium contaminated groundwater at a Department of Energy facility near Monticello, Utah. Not the limited visual impact of the PRB emplacement.

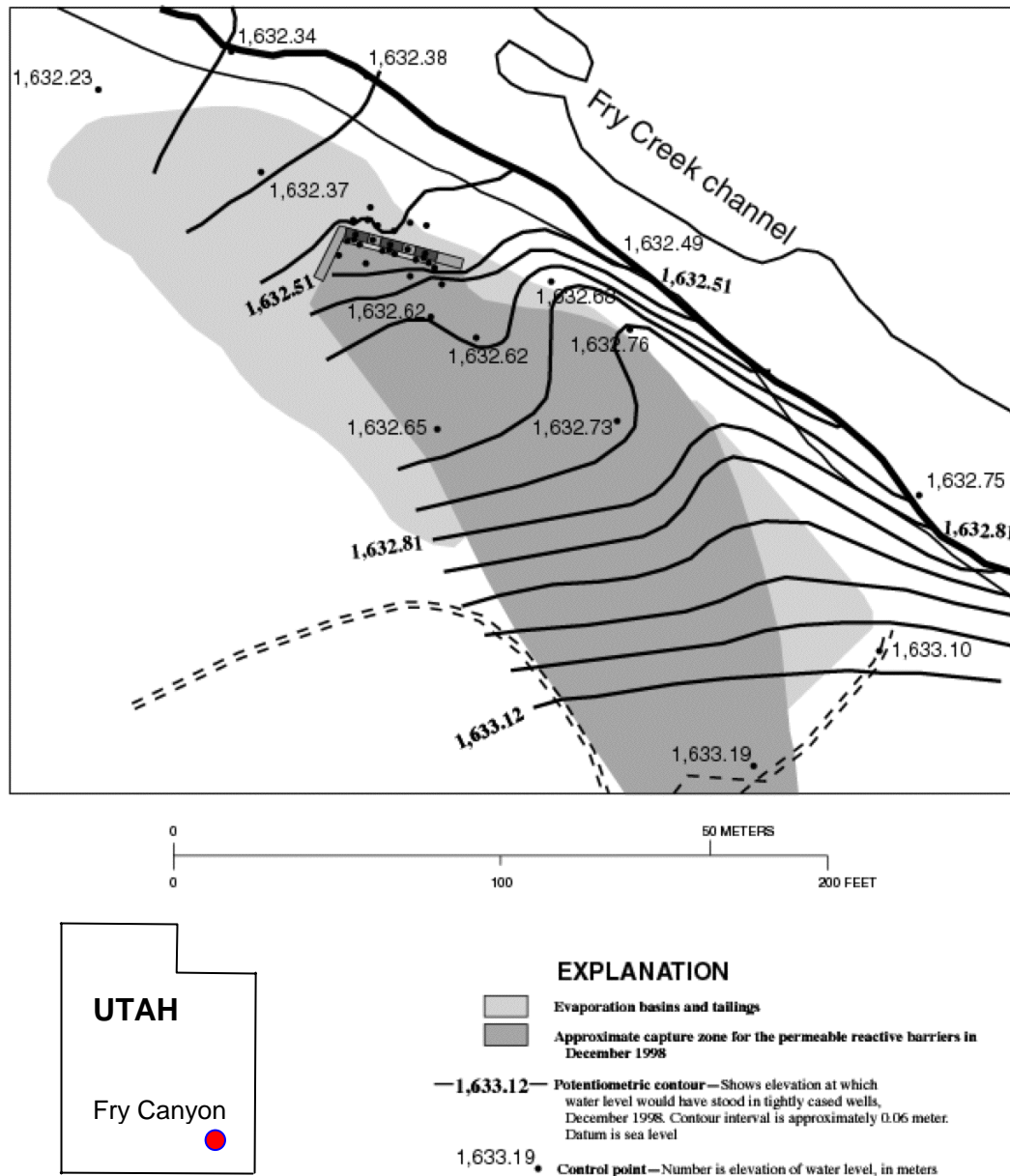


Figure 2. Location of Fry Canyon permeable reactive barrier demonstration site in southeastern Utah.

As an example of mining-related waste, historical uranium exploration, mining, and milling operations have resulted in elevated U concentrations in many aquifers (Landa and Gray, 1995). The Fry Canyon site (fig. 2) was selected in 1996 as a field-scale demonstration site to assess the feasibility of treating U-contaminated groundwater with PRBs (Naftz et al., 1999; Naftz et al., 2000). This paper will present performance results of a zero-valent iron (ZVI) PRB during a 10-year operating period (1997-2006), including: (1) uranium distributions and removal efficiencies; (2) changes in groundwater flow velocities; and (3) isotopic evidence of bacterially mediated sulfate reduction during PRB aging.

Site Description

The Fry Canyon site was constructed and operated by COG Minerals Cooperation and is located on BLM managed land. The purpose of the facility was to upgrade U from ore obtained primarily from three U mines in the White Canyon Mining District of southeastern Utah. The upgraded material was then transported about 115 kilometers (km) to the Texas-Zinc Minerals Corporation mill at Mexican Hat, Utah.

The upgrader operated during 1957-60 and processed about 45,400 metric tons of ore containing between 0.10 and 0.15 percent (%) U_3O_8 (Utah Department of Health, 1987). Water for the operation was supplied from a large-diameter well completed in the colluvial material within and adjacent to Fry Creek (fig. 2). About 36,000 metric tons of sand tailings, containing about 0.02% U_3O_8 , were impounded on the site by the time the upgrader was closed.

In 1962, the Fry Canyon site and associated water rights were acquired by the Basin Company for a copper (Cu) heap leaching operation. This operation used sulfuric acid to leach the Cu into solution. The Cu was subsequently precipitated with hydrogen sulfide and collected on pieces of scrap iron (Fe), some of which is still at the site. The Cu extraction operations ceased in 1968. The site remained inactive until 1997, when three PRBs were installed at the site for field demonstration U removal from contaminated groundwater (Naftz et al., 1999; Naftz et al., 2000; Naftz et al., 2002; and Rowland, 2002).

As a result of the U upgrading and Cu extraction operations at the site, the shallow colluvial aquifer adjacent to Fry Creek was contaminated. The concentration of U in groundwater from the colluvial aquifer can exceed 20,000 micrograms per liter ($\mu\text{g/l}$) (Naftz et al., 2002). The high alkalinity (mean = 400 milligrams per liter (mg/l) as CaCO_3) coupled with measurable amounts of dissolved oxygen in the contaminated groundwater indicate that U is likely to be in the +6 oxidation state as a carbonate species. These U concentrations are substantially higher than background U concentrations, which range from 60 to 80 $\mu\text{g/l}$.

Results and Discussion

Uranium Removal Efficiencies

The ZVI PRB has been in continuous operation since 1997 at the Fry Canyon demonstration. The reactive material used in the ZVI PRB was Cercona iron foam pellets. The foam pellets had high hydraulic conductivity values (122 to 250 m/d) and high laboratory removal efficiencies from groundwater containing 2,100 $\mu\text{g/l}$ dissolved U (Naftz et al., 2000). One possible mechanism for U removal from solution during interaction with the ZVI reactive material is

chemical reduction of U(VI) to U(IV) and subsequent precipitation (Gu et al., 1999).

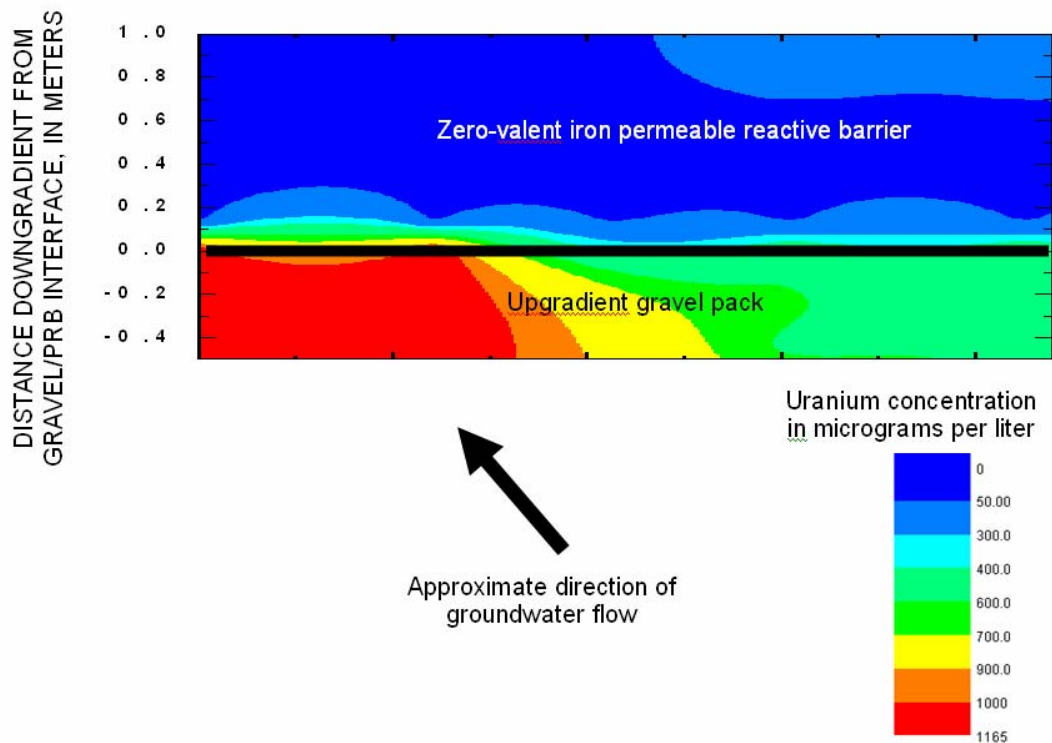


Figure 3. Distribution of dissolved uranium concentration in the upgradient gravel pack and downgradient zero-valent iron permeable reactive barrier during April 2005 at Fry Canyon, Utah.

Periodic monitoring of the incoming and treated groundwater in the ZVI PRB during the demonstration period from 1997 through 2005 indicates virtually 100 % removal of U. Evidence of long-term U removal in the ZVI PRB is shown from the contour map of U concentration in water samples collected during April 2005 (fig. 3). After flowing approximately 0.3 m into the ZVI PRB, the concentration of U is reduced to < 50 ug/L, with most water < 20 ug/L. The small increase in dissolved U concentration within the downgradient part of the PRB is likely due to the inflow of untreated groundwater due to the low hydraulic gradients associated with the PRB demonstration site.

Uranium removal ratios (URR), unitless, were used for comparison of U-removal efficiencies to detect early signs of PRB failure during 1997 through 2005 (fig. 4). The URR for flow paths 1 and 2 in the ZVI PRB was calculated by

$$URR = 1 - (U_{15 \text{ cm}} / U_{\text{influent}}), \quad (1)$$

where, $U_{15 \text{ cm}}$ is the U concentration in treated groundwater after traveling about 15 cm through the reactive material and U_{influent} is the U-influent concentration into the ZVI PRB. The shortest possible flow path was used because the

upgradient section of each PRB will likely be the most sensitive to changes in contaminant removal efficiencies. A URR of 1.0 indicates complete (100%) U removal; whereas a URR less than 0.0 indicates that the U is being mobilized from the reactive material. The URRs for both flow paths in the ZVI PRB were consistently near 1.0 (fig. 4), indicating high U removal efficiencies and no indication of PRB failure.

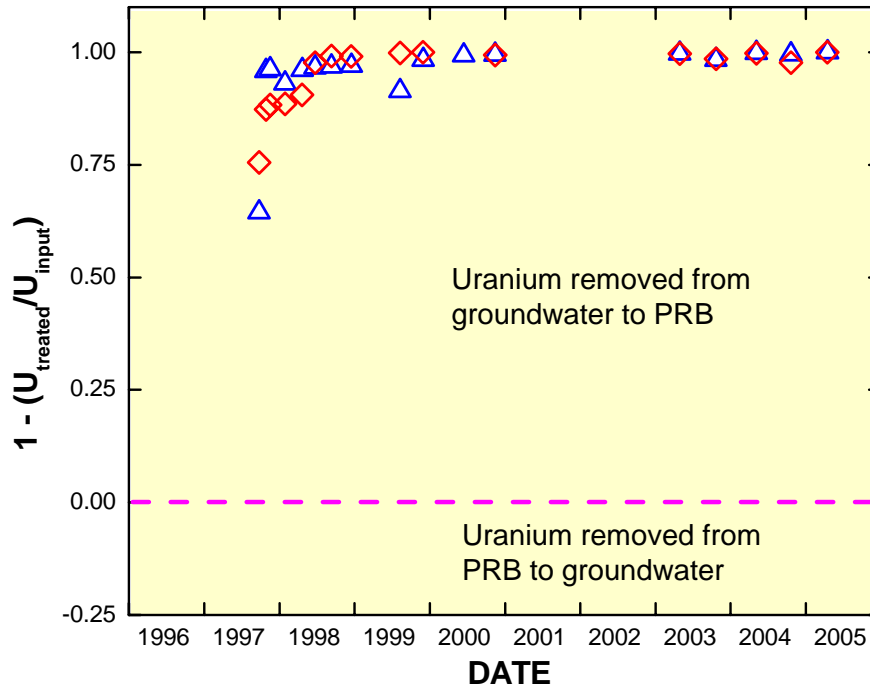


Figure 4. Uranium removal ratios after groundwater has traveled 0.15 m into the zero-valent iron permeable reactive barrier at Fry Canyon, Utah.

Changes in Groundwater Velocity

Ionic tracer tests conducted in the ZVI PRB indicate a decrease in groundwater velocities, from an average of 1.54 meters/day (m/d) in 1999 to 0.95 m/d in 2003 and 0.4 m/d in 2005. Additional hydrologic and geochemical data are being collected to better understand the velocity trends. Potential processes that could lead to the observed reduction in groundwater velocities in ZVI PRBs include mineral precipitates such as iron hydroxides, carbonates, and sulfides (Gu et al., 1999; Li et al., 2006), as well as hydrogen gas production and entrapment (Reardon, 2005),.

Aerobic and anaerobic corrosion of ZVI can result in large increases in the pH of the groundwater after entering the PRB (Morrison et al., 2002) Depending on the groundwater chemistry, the pH increase can result in mineral precipitation.

Cores collected from the ZVI PRB during May 1999 indicate that mineral precipitation is occurring. Minerals qualitatively identified in those cores included iron sulfide, calcite, and metallic iron (Naftz et al., 2002). In a series of laboratory column experiments, Gu et al. (1999) identified a number of mineral precipitates forming in ZVI material. Mineral precipitates included iron hydroxides, carbonates, and sulfides.

Total dissolved gas pressure (TDG) pressure was measured in wells upgradient and within the ZVI PRB at Fry Canyon during April 2006. The purpose of these measurements was to evaluate relative changes in TDG pressure moving from upgradient wells outside of the ZVI PRB to wells within the PRB and to relate these changes to potential production and build up of hydrogen gas in the reactive barrier. The TDG pressure of selected wells within the ZVI PRB increases by over 100 mm Hg relative to the upgradient wells outside of the PRB (fig. 5). Although the TDG results may indicate the production and build up of hydrogen gas, more quantitative and gas-specific data are required. Concurrent with the TDG measurements, passive diffusion gas samplers were deployed in selected wells and are currently (August 2006) being analyzed for dissolved gas composition (hydrogen, argon, nitrogen, helium, neon, and xenon).

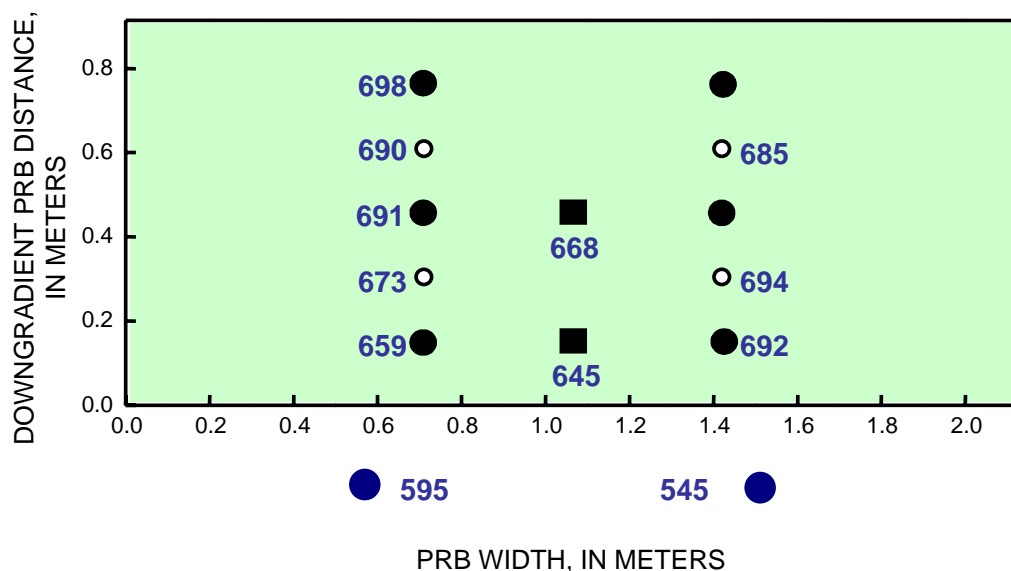


Figure 5. Total dissolved gas pressure (in millimeters of mercury) measured upgradient and within the zero-valent iron permeable reactive barrier (PRB) during April 2006, Fry Canyon, Utah.

Sulfate Reduction

Anerobic corrosion of metallic iron can produce hydrogen gas ($H_{2(g)}$), which can then be utilized by sulfate-reducing bacteria (SRB) to chemically reduce sulfate and form iron sulfide mineral phases (Rowland, 2002). As noted in

the previous section, the formation of iron sulfides is one of the mineral precipitation reactions that can contribute to ZVI PRB plugging and subsequent reductions in longevity. Long-term monitoring of sulfate concentrations in the ZVI PRB at Fry Canyon indicates increased amounts of sulfate removal over time (fig. 6). Although the influent sulfate concentration can be highly variable, the increasing proportions of sulfate that is removed by the PRB is likely related to increasing amounts of bacterially mediated sulfate reduction.

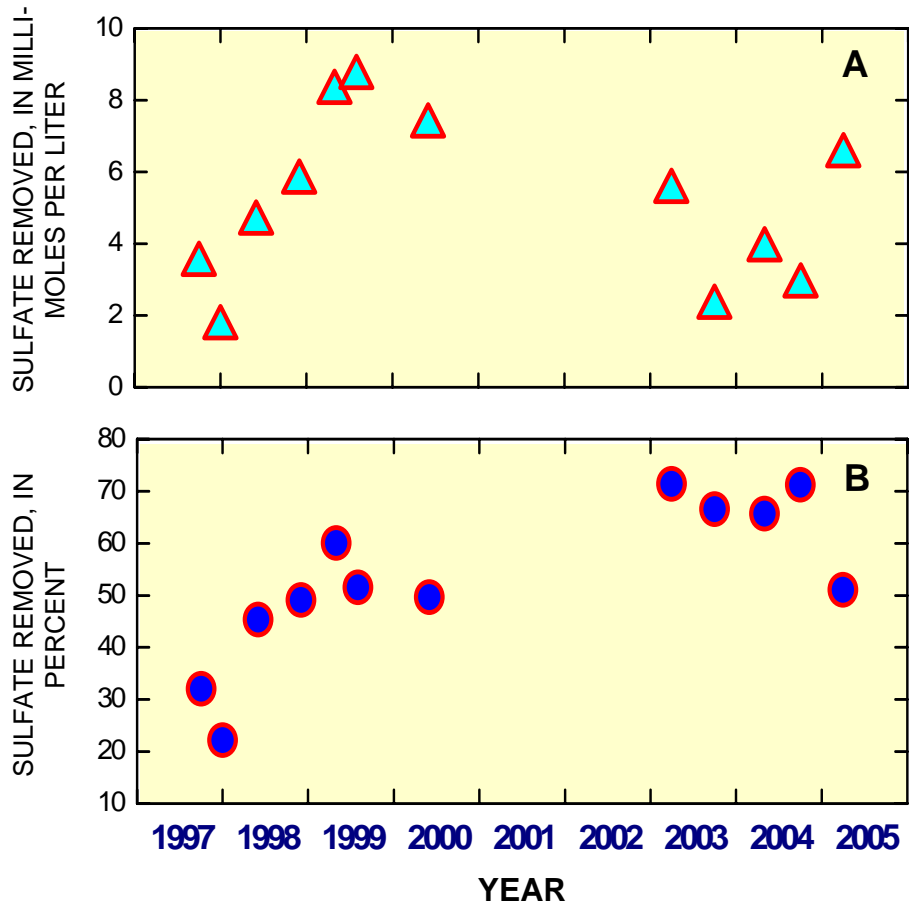


Figure 6. Changes in mass (A) and percent (B) of sulfate removed in the zero-valent iron permeable reactive barrier from 1997 to 2005. Sulfate removal calculated using sulfate concentration in influent water and treated water after traveling 0.3 meters into the permeable reactive barrier.

Stable isotopes of sulfur and oxygen in the sulfate anion from groundwater samples were used to investigate how the amount of bacterially mediated sulfate reduction has changed over time, as well as the potential changes in input sulfate source(s). The SRB preferentially utilize the isotopically light ^{32}S in the dissolved sulfate, resulting in an isotopic enrichment of the ^{34}S in the residual sulfate. Laboratory investigations have shown that SRB can produce enrichments in $\delta^{34}\text{S}$

in the remaining sulfate of 10 to 46 permil, with an average enrichment of 25 permil (Kaplan and Rittenberg, 1964; Kemp and Thode, 1968; Nakai and Jensen, 1964; Clark and Fritz, 1997; and Canfield 2001).

The $\delta^{34}\text{S}$ value of the dissolved sulfate was determined in samples of groundwater from upgradient and within the ZVI PRB during 2000, 2004, and 2005 (fig. 7). With the exception of one sample collected in 2000, the $\delta^{34}\text{S}$ of the residual dissolved sulfate becomes more enriched as the sulfate concentration decreases, indicative of isotopic fractionation by SRB. During 2000, the $\delta^{34}\text{S}$ of dissolved sulfate was found to be enriched by 23.6 permil relative to the $\delta^{34}\text{S}$ of dissolved sulfide from the same well in the ZVI PRB (Rowland, 2002).

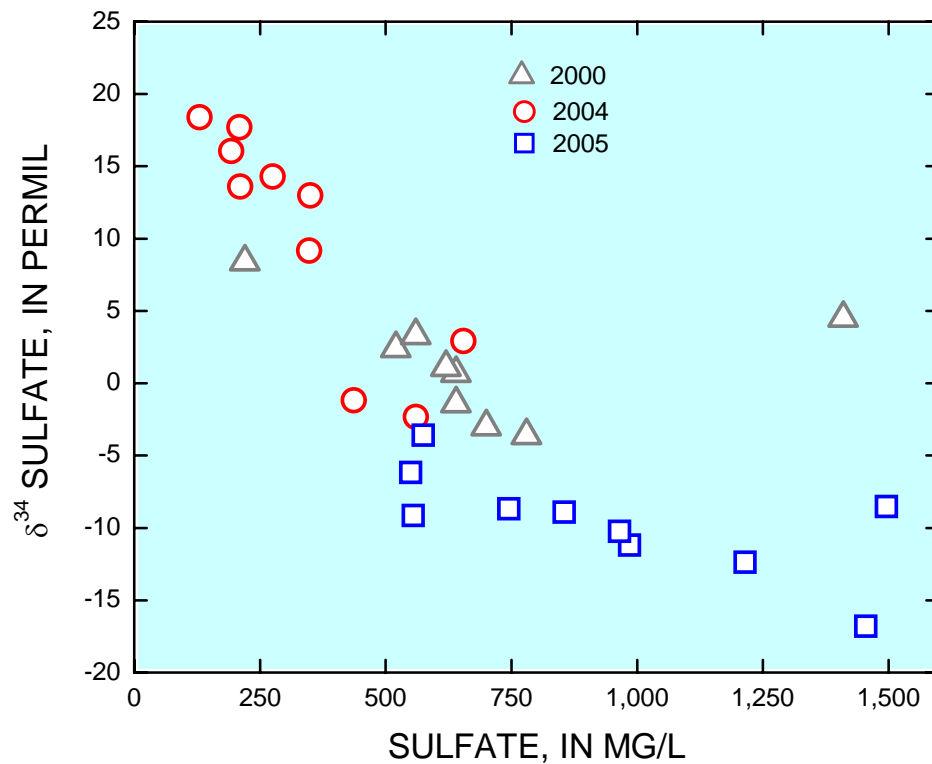


Figure 7. Change in the delta sulfur-34 ($\delta^{34}\text{S}$) of dissolved sulfate with changes in sulfate concentration in groundwater samples collected from wells located upgradient and within the zero-valent iron permeable reactive barrier during 2000, 2004, and 2005, Fry Canyon, Utah.

The most enriched residual $\delta^{34}\text{S}$ of the dissolved sulfate (+18.39 permil) in a downgradient well within the ZVI PRB was observed from samples collected during 2004 (fig. 7). Approximately one year later, the most enriched residual $\delta^{34}\text{S}$ of dissolves sulfate was significantly lighter (+3.59 permil). This difference between residual $\delta^{34}\text{S}$ of dissolved sulfate between 2004 and 2005 does not

represent a difference in the efficiency of sulfate reduction occurring in the ZVI PRB, but rather a significant change in the source of dissolved sulfate entering the reactive barrier. Relative to the samples collected in 2005, influent groundwater collected in 2004 contained a significantly lower concentration of dissolved sulfate (approximately 500 mg/L) and isotopically enriched $\delta^{34}\text{S}$ value of dissolved sulfate (approximately 0 permil) (fig. 7). Hydrologic data supporting a different source of sulfate entering the ZVI PRB is indicated by an increase in groundwater level of 0.2 m in upgradient wells between 2004 and 2005, suggesting the resaturation of previously dry alluvial sediments.

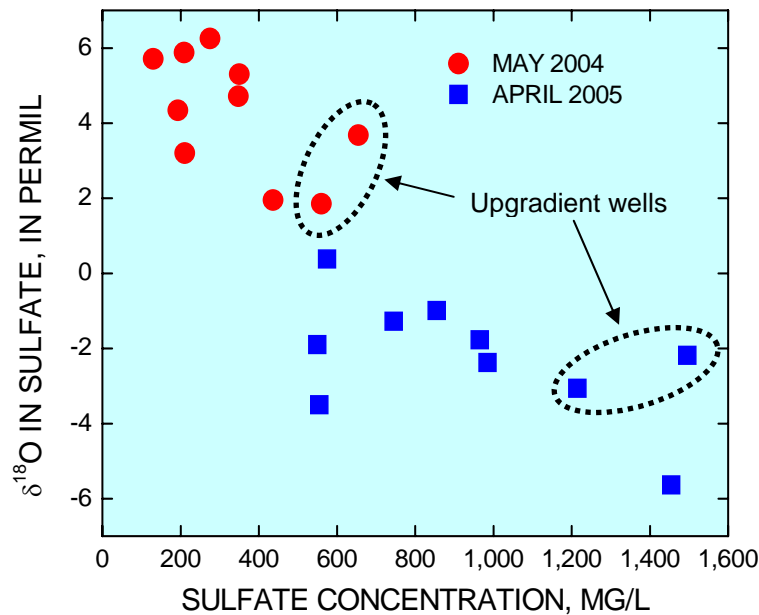


Figure 8. Change in the delta oxygen-18 ($\delta^{18}\text{O}$) of dissolved sulfate with changes in sulfate concentration in groundwater samples collected wells located upgradient and within the zero-valent iron permeable reactive barrier during 2004 and 2005, Fry Canyon, Utah.

The $\delta^{18}\text{O}$ of the dissolved sulfate in the influent water entering the ZVI PRB also indicates a distinct difference between 2004 and 2005 (fig. 8). The $\delta^{18}\text{O}$ of dissolved sulfate provides important information on the source and pathway of sulfate in the environment (Holt and Kumar, 1991). The rate of abiotic oxygen isotope exchange between water and dissolved sulfate is extremely low, hence once the sulfate mineral phase is formed, the $\delta^{18}\text{O}$ value of the sulfate is likely preserved (Holt and Kumar, 1991). The lighter $\delta^{18}\text{O}$ values of dissolved sulfate in source waters entering the ZVI PRB during 2005 likely reflect the dissolution of sulfates that may have previously formed from the sulfuric acid used for copper extraction at the Fry Canyon site. In contrast, the heavier $\delta^{18}\text{O}$ values of dissolved

sulfate in the 2004 source waters could be reflective of the natural sulfate sources in the Fry Canyon area.

Bacterial reduction of sulfate will enrich the isotopic composition of oxygen in the residual dissolved sulfate. The SRB preferentially metabolize the lighter isotope of oxygen, thereby enriching the $\delta^{18}\text{O}$ value of the residual sulfate (Holt and Kumar, 1991). Once the source water enters the ZVI PRB, the observed enrichment of $\delta^{18}\text{O}$ values in the residual sulfate (fig. 8) supports bacterially mediated sulfate reduction during the 2004 and 2005 monitoring periods. Bacterially mediated sulfide production in the ZVI PRB would likely remove other trace metals, if present in the input water, by the formation of metal sulfides. Increasing amounts of iron sulfide formation is evident at the Fry Canyon site by the significant reduction in the export of dissolved iron from the ZVI PRB.

Acknowledgements

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Literature Cited

- Canfield, D.E., 2001. Isotope fractionation by natural populations of sulfate-reducing bacteria. *Geochim. Cosmochim. Acta*. **65**, 1117-1124.
- Clarke, I., and Fritz, P., 1997. Environmental isotopes in hydrogeology. Lewis Publishers, New York.
- Gu, B., Phelps, T.J., Liang, L., Dickey, M.J., Roh, Y., Kinsall, B.L., Palumbo, A.V., and Jacobs, G.K., 1999. Biogeochemical dynamics in zero-valent iron columns: Implications for permeable reactive barriers. *Environ. Sci. Tech.* **33**, 2170-2177.
- Holt, B.D., and Kumar, R., 1991. Oxygen isotope fractionation for understanding the sulphur cycle in Krouse, H.R., and Grinenko, V.A., eds., Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, John Wiley and Sons, New York, New York, p. 27-41.
- Kaplan, I.R., and Rittenberg, S.C., 1964. Microbiological fractionation of sulphur isotopes. *J. Gen. Microbiol.* **34**, 195-212.
- Kemp, A.L., Thode, H.G., 1968. The mechanism of the bacterial reduction of sulphate and sulphite from isotopic fractionation studies. *Geochem. Cosmochim. Acta* **32**, 71-91.

Landa, E.R., and Gray, J.R., 1995. U.S. Geological Survey research on the environmental fate of uranium mining and milling wastes: *Environmental Geology* **26**, 19-31.

Li, L., Benson, C.H., and Lawson, E.M., 2006. Modeling porosity reductions caused by mineral fouling in continuous-wall permeable reactive barriers. *Journal of Contaminant Hydrology*, vol. 83, p. 89-121.

Morrison, S.J., Naftz, D.L., Davis, J.A., and Fuller, C.C., 2002, Introduction To Groundwater Remediation of Metals, Radionuclides, and Nutrients, with Permeable Reactive Barriers, *in* Naftz, D.L., Morrison, S.J., Davis, J.A., and Fuller, C.C. eds., *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*, Academic Press, New York, New York, p. 1-19.

Naftz, D.L., Davis, J.A., Fuller, C.C., Morrison, S.J., Freethey, G.W., Feltcorn, E.M., Wilhelm, R.G., Piana, M.J., Joye, J.L., and Rowland, R.C., 1999. Field demonstration of permeable reactive barriers to control radionuclide and trace-element contamination in ground water from abandoned mine lands. *In* "U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999. Contamination from Hardrock Mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A" (Morganwalp, D.W., and Buxton, H.T., eds.), Vol. 1, pp. 281-288.

Naftz, D.L., Fuller, C.C., Morrison, S.J., Davis, J.A., Freethey, G.W., Rowland, R.C., Piana, M.J., Feltcorn, E.M., Wilhelm, R.G., and Blue, J.E., 2000. Field demonstration of permeable reactive barriers to remove dissolved uranium from groundwater, Fry Canyon, Utah, September 1997 through September 1998, Interim report. U.S. Environmental Protection Agency Report EPA 402-C-00-001.

Naftz, D.L., Fuller, C.C., Davis, J.A., Morrison, S.J., Feltcorn, E.M., Rowland, R.C., Freethey, G.W., Wilkowske, C., and Piana, M., 2002, Field Demonstration of Three Permeable Reactive Barriers to Control Uranium Contamination in Groundwater, Fry Canyon, Utah, USA, *in* **Naftz, D.L.**, Morrison, S.J., Davis, J.A., and Fuller, C.C. eds., *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*, Academic Press, New York, New York, p. 401-434.

Nakai, N., Jensen, M.L., 1964. The kinetic isotope effect in the bacterial reduction of and oxidation of sulfur. *Geochim. Cosmochim. Acta* **65**, 223-235.

Reardon, E.J., 2005. Zerovalent irons: Styles of corrosion and inorganic control on hydrogen pressure buildup. *Environmental Science and Technology*, vol. 39, p. 7311-7317.

Rowland, R.C., 2002, Sulfate-reducing bacteria in the zero-valent iron permeable reactive barrier at Fry Canyon, Utah, *in* Naftz, D.L., Morrison, S.J., Davis, J.A., and Fuller, C.C. eds., *Handbook of Groundwater Remediation Using Permeable Reactive Barriers: Applications to Radionuclides, Trace Metals, and Nutrients*, Academic Press, New York, New York, p. 281-304.

U.S. Geological Survey Abandoned Mine Lands Science Team, 1999. Abandoned Mine Lands Initiative—Providing Science for Watershed Issues. *In* U.S. Geological Survey Open-File Report 99-321. (P.J. Modreski, Compiler), pp. 29-30.